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Solvents for Gold

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A STUDY OF SOLVENTS FOR GOLD

BY

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THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

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Solvents for Gold.

That gold defies the attacks of most reagents and is indifferent to their action is a fact known to all chemists. The inactive character of gold is due to the fact that only under certain favorable conditions is it oxidized. The solvents for gold in general use to-day are chlorine, bromine and potassium cyanide. There are numerous other solvents which will be mentioned later. Iodine attacks gold only when it is freshly liberated. The affinity of chlorine for gold is very great and it attacks gold with great avidity when brought in contact with the metal. The chlorine forms a soluble chloride of gold ($Au\ Cl_3$). That chlorine does attack gold and forms a soluble chloride has long been known, but it was not until 1858 that it was introduced into the United States by Plattner as a practical means of extracting gold from the ores.

2. The solubility of gold in a solution of potassium cyanide has been a known fact for a number of years. Hagen mentioned it in 1806. Gold cyanide solution was used in 1840 by Dr. Wright of Birmingham, England for electroplating. The first record in scientific literature of experiments in which metallic gold was dissolved in a potassium cyanide solution consists in Prince Pierre Bagraton's paper in the Bulletin d l' Academie Imperiale des Sciences de St. Petersbourg 1843. t. II, P.136. Bagraton preserved potassium cyanide solution in a dish gilded on the inside. After several days he noticed that the whole inside had been attacked. He also found that the electric current had no influence on the solvent action, and that the dissolved gold could be precipitated on copper or sil-

ver plates by means of the electric current. Bagraton noticed that oxygen was necessary to the solution of gold in cyanide solution, and he also made the statement that heat hastened the solvent action of the solution. This last statement does not seem to be born out by later experiments. That oxygen is necessary to the solution of gold in a known fact and means are resorted to to keep the solution in agitation in order to keep plenty of atmospheric oxygen in the solution.

The chemical action which takes place when gold dissolves in a potassium cyanide solution is as follows:

$$2Au + 4KCN + O + H_2O = 2KAuCN_2 + 2KOH \quad (3)$$

A double cyanide of gold and potassium is formed which is easily dissolved in water. The cyanide solution was not put to a practical use until 1889 when MacArthur and Forrest of Glascow, Scotland took out an English patent for the process. A patent was taken out for the cyanide solution in the United states as early as 1867, but no practical commercial results were obtained until 1889 when MacArthur and Forrest had their process patented.

4 A word as to the part taken by oxygen in the solution of gold in the cyanide solution will not be out of place here. Faraday indicates clearly that air contact and the formation of air voltaic circles are necessary for the reaction. He does not infer that any oxidizing action is necessary. He says air voltaic cells are formed in these cases and the gold is dissolved almost exclusively under their influence. When one piece of gold leaf was placed on the surface of a solution of cyanide of potassium, and another, moistened on both sides, was placed under the surface, both dis-

solved; but twelve minutes sufficed for the solution of the first whilst about twelve hours were required for the submerged piece. In weaker solutions, and with silver also the same results were obtained; from sixty to a hundred fold as much time being required for the disappearance of the submerged metal as for that which, floating, was in contact both with air and the solvents.

5. Victor Lenher, of the University of Wisconsin, has recently done work on solvents for gold which he published in the Journal of the American Chemical Society for May 1904, under the title, Solubility of Gold in Certain Oxidizing Agents. Lenher experimented with substances which evolved oxygen when treated with an acid and found that quite a number of them dissolved gold. His work with Telluric acid led him to experiment with the different substances which evolve oxygen when treated with an acid. Telluric acid at the temperature at which it dissolves gold is broken down into the dioxides and oxides. From this it appeared probable that the solvent action in these cases was due to the production of oxygen in the reaction. If this is the case any reagent that will give off oxygen should attack gold. Lenher tried a number of substances, such as the oxides of various metals and sulphates with sulphuric, phosphoric and arsenic acids and found that only such substances as produce oxygen in the presence of acids will act on the gold. The chemicals used were all tested for the halogens and only those which were halogen free were used.

Manganese dioxide was the first substance experimented on. This oxide when treated with sulphuric acid evolves oxygen. Gold is dissolved when heated slightly with this mixture and may be precipitated by means of ferrous sulphate. The above action also

takes place in the cold, an appreciable amount being dissolved at 0° centigrade.

Manganese sesquioxide (Mn_2O_3), manganese protosesquioxide (Mn_3O_4) and potassium permanganate attack gold in the presence of concentrated sulphuric acid. Phosphoric and arsenic acid may be substituted for sulphuric acid, but the action is much slower. In 1872 Allen showed that when solid potassium permanganate and sulphuric acid are heated for a few minutes with precipitated gold, the solution becomes clear, the gold disappearing. On diluting and treating with ferrous sulphate the gold was precipitated. Lenher found that phosphoric acid could be substituted for sulphuric acid.

Lead dioxide, lead sesquioxide and red lead, when used with sulphuric acid, cause gold to go into solution. The action takes place more readily in the warm than in the cold, though at ordinary temperature solution does take place. Heat, however, accelerates the action. Phosphoric acid may be substituted for sulphuric acid with the higher oxides of lead, solution being effected. Both phosphoric and sulphuric acids effect the solution of gold with chromium trioxide, chromium tetraoxide and nickelic oxide. The reactions in the above cases take place in the cold, but rather feebly. A hot mixture of nitric and sulphuric acids will dissolve gold. This is due to the fact that nitric acid is more or less decomposed when heated; nitrogen dioxide and oxygen being formed. When the gold goes into solution a lower oxide of nitrogen is formed by the reduction of the nitric acid and this oxide remains in solution. Spiller showed that a lower oxide of nitrogen is formed by adding water to the solution when the gold is thrown out as a beautiful purple precipitate, the purple of Cassius is thrown out. This pre-

cipitation from the nitric-sulphuric acid solution is due to the presence of a lower oxide of nitrogen, probably nitrous acid, for when the water used for dilution contains potassium permanganate no precipitation takes place.

5 Reynolds, Spiller and Allen have studied the action of a mixture of nitric and sulphuric acids on gold, but did not pay any attention to the temperature. Lenher observed the temperature when he experimented with a mixture of nitric and sulphuric acids. He found that the action is hastened by the application of heat, but that a perceptable amount of gold is dissolved even at a temperature of 0° centigrade. He also found that phosphoric acid could be substituted for sulphuric in the mixture. Neither oxygen gas nor ozone effect the solution of gold in hot sulphuric acid solution.

That anode oxygen, obtained by the electrolysis of water, acts on gold was noticed by Bunsen. He noticed that in the electrolysis of water, using platinum electrodes, fastened to the terminals with gold solder, that a film of oxide formed on the gold. Spiller showed that when a plate of metallic gold is used as the anode and a piece of platinum foil is used as the cathode in an electrolyte of sulphuric acid, the gold anode dissolved and the metal was deposited on the cathode. This also takes place when a mixture of sulphuric and nitric acids are used. When the acid is dilute the oxide of gold formed does not pass into solution, but remains as a coating on the gold anode. This work which has been performed many times shows that solution of gold can be readily effected by means of anode oxygen in the presence of sulphuric acid. Lenher substituted phosphoric acid for sulphuric and obtained

similar results. When the electrolytes consist of acid, sulphates of potassium or sodium, the action is the same as above. If plenty of free acid is present the gold passes through the solution and is deposited on the cathode. If the solution contains little free acid the gold remains in the form of oxide on the anode. In an electrolyte of sodium or potassium hydroxide some of the gold passes through the solution and is deposited on the cathode, while a larger portion remains as an incrustation of oxide on the anode. When nitrates or sulphates of sodium or potassium are used, very little, if any, gold passes through the solution, but remains on the anode as the oxide (Au_2O_3). This is due to the fact that the solution is neutral.

A great deal has, no doubt, been done along this line, but very little has been published, due to the fact that the results obtained, have not been very satisfactory. The historical part of this paper, on this account, is necessarily brief.

My first work in the laboratory consisted mainly of testing the solubility of gold, using the reagents mentioned by Lenher in his article on the Solubility of Gold in Certain Oxidizing Agents, published in the May number of the Journal of the American Chemical Society. Numerous reagents, other than those mentioned by Lenher, were tested. These tests were run, observing the condition of the reaction; temperature, time required and concentration.

The gold used in the following tests was leaf gold, cut in circular pieces weighing .0004 grams. A good surface was thus exposed to the action of the solvent. A mixture of equal portions of concentrated nitric and sulphuric acids was thus considered first.

This mixture was allowed to act on gold at the temperature of the laboratory, 22° centigrade, the gold leaf not being added until the mixture attained the temperature of the room. At this temperature, to dissolve the entire disc, required sixteen hours. After standing seventeen hours at a temperature of approximately 0° centigrade, the nitric-sulphuric acid mixture had dissolved enough of the gold to be detected. As the temperature increases, the solvent action of the mixture increases until at the boiling point of the mixture, disappears almost instantaneously. The solubility of gold in a mixture of nitric and sulphuric acids is due to the fact that nitric acid breaks down to a certain degree into nitrogen dioxide and oxygen. The sulphuric acid aids this decomposition. The gold is precipitated from the solution when water is added.

Red lead (Pb_3O_4) when treated with sulphuric acid gives off oxygen, according to the equation: $Pb_3O_4 + 3H_2SO_4 = PbSO_4 + 3H_2O + O$. 6 This oxygen, as it is being evolved, attacks gold and renders it soluble. The action is perceptable after long standing at ordinary temperatures, but heat is necessary to a rapid solution of the gold. At the temperature of the laboratory it was necessary to leave the gold in contact with the solution for eight hours before gold could be detected in the solution. At temperatures lower than 22° centigrade no gold could be detected in the solution.

Lead peroxide (PbO_2) in the presence of sulphuric acid is a solvent for gold. This is due to the fact that oxygen is disengaged. $2PbO_2 + 2H_2SO_4 = 2PbSO_4 + 2H_2O + O_2$. 6

At the ordinary temperature the solvent action is very slow; heat hastening the action. The behavior of a sulphuric acid mix-

ture of this oxide toward gold is similar to that given above for red lead.

Lead oxide (PbO) has no solvent action on gold.

Pb_2O_3 and sulphuric acid attack gold. The conditions of the actions are similar to those of the other oxides; slow at low temperatures with an increase of activity as the temperature rises.

$$2Pb_2O_3+4H_2SO_4=4PbSO_4+4H_2O+O_2. \quad 6$$

Potassium permanganate ($KMnO_4$)and sulphuric acid act on gold quite readily. At ordinary temperatures gold can be detected after a contact of twenty-five or thirty minutes and on standing longer the disc is entirely dissolved. The boiling mixture dissolves the gold at once. At a temperature of about 0° centigrade no gold could be detected. The solvent action of this mixture is due to the solvent action of oxygen; potassium permanganate being a strong oxidizing agent:

$$2KMnO_4+3H_2SO_4=2MnSO_4+K_2SO_4+3H_2O+5O. \quad 6$$

The gold may be precipitated from this solution by means of ferrous sulphate ($FeSO_4$). Enough ferrous sulphate must be added to reduce the excess of potsssium permanganate before precipitation takes place.

Manganese dioxide (MnO_2) when treated with sulphuric acid acts in the following manner:

$$2MnO_2+2H_2SO_4=2MnSO_4+2H_2O+O. \quad 6$$

This liberated oxygen attacks gold and renders it soluble. The action is quite rapid at the ordinary temperature. Increase in temperature accelerates the action. At 0°centigrade, enough gold is dissolved off after ten or twelve hours to be easily detected.

Manganese heptoxide(Mn_2O_7) an oily liquid formed when cold sulphuric acid acts on potassium permanganate attacks gold. This reagent is such a powerful oxidizing agent that paper, alcohol and other organic matter are inflamed by mere contact with it.

As was stated above iodine attacks gold when freshly liberated. This is the case when sulphuric acid acts on potassium iodide(KI). Reaction is very slow at ordinary temperatures and it is only after long standing that gold can be detected in the solution.

Potassium dichromate, or red chromate of potash ($K_2Cr_2O_7$) is an oxidizing agent in the presence of acids according to the following equations:

$$K_2Cr_2O_7+4H_2SO_4=Cr_2(SO_4)_3;K_2SO_4+4H_2O+3O. \quad 6$$

When heated it melts and at high temperatures it decomposes into potassium chromate, chromic oxide, and oxygen:

$$2K_2Cr_2O_7=2K_2CrO_4+Cr_2O_3+3O. \quad 6$$

It is this freshly liberated oxygen that attacks the gold and renders it soluble. The action of the mixture on gold takes place in the cold, but heat increases the action, due to the fact that hot sulphuric acid acts more vigorously, and that heat aids in the formation of oxygen. from the dichromate.

Potassium dichromate and a solution of salt (NaCl) will dissolve gold.

Potassium persulphate ($K_2S_2O_8$) on being heated yields oxygen and the pyrosulphate ($K_2S_2O_7$) is formed. This oxygen is liberated in the presence of acids and when gold is brought into the solution it is dissolved.

Chromic oxide (Cr_2O_3) and chromium trioxide (CrO_3) were experimented with, but as special work was done with chromium tri-

oxide its action will be considered later. A list of the solvents, those mentioned above and others, is as follows:

Those having an oxidizing effect are:

$HNO_3+H_2SO_4$ 7.
$KMnO_4+H_2SO_4$ 7.
$Pb_2O_3+H_2SO_4$ 7.
$CrO_3+H_2SO_4$ 7.
$K_2S_2O_8+H_2SO_4$ 8.
$Mn_2O_7+H_2SO_4$ 8.
$K_2Cr_2O_7+NaCl$ 8.
H_2TeO_4(Telluric acid) 7.
$Pb_3O_4+H_2SO_4$ 7.
$MnO_2+H_2SO_4$ 7.
$PbO_2+H_2SO_4$ 7.
$Cr_2O_3+H_2SO_4$ 7.
$K_2Cr_2O_7+H_2SO_4$ 8.
$(NH_4)_2S_2O_8+H_2SO_4$ 8.
$K_2Cr_2O_7+CaCl_2$ 8.
H_2SeO_4(Selenic acid) 7.

Those having effect other than oxidizing are:

MnO_2 HCl(Due to Cl) 7.
$K_2S_2O_8$ HCl (Cl liberated)
$KI+H_2SO_4$(Due to I) 7.
KCN A double 3.
7. K_2S Slight solvent action.cyanide of gold being formed
Na_2S.

Mercury (H g) may be considered as a solvent for gold as it forms an alloy with it which is called an amalgam.

Observations made using a solution of chromium trioxide(CrO_3) and a solution of common salt (NaCl).

9. Classen mentions the fact that a solution of chromium trioxide and common salt will dissolve gold, in his text on Quantitative Chemical Analysis by Electrolysis. He simply mentions the fact that a solution of chromium trioxide and a saturated solution of sodium chloride is a good means of dissolving gold from platinum electrodes in the quantitative analysis of gold. He does not attempt to explain the action. This I will attempt to do after

giving the data of some of the work performed in the laboratory. My first work on a mixture of chromium trioxide solution and sodium chloride solution was to determine the concentration of the mixture which would be the most effective, also the temperature at which the action was most rapid. The following data was obtained:

SOLUTION	TEMPERATURE	TIME
IO c.c. CrO_3 IO% IO c.c.NaCl 20%	25° Centigrade	1 hour 32 minutes.
"	" "	1 " 27 minutes.
"	" "	1 " 39 "
"	" "	1 " 29 "
"	" "	1 " 36 "
10 c.c. CrO_3 IO% IO c.c.NaCl 20%	35° Centigrade	1 hour 7 minutes.
"	" "	1 " 3 "
"	" "	1 " 12 "
"	" "	1 " 9 "
"	" "	1 " 57 "

The temperature in the last case going above 35°Centigrade.

SOLUTION	TEMPERATURE	TIME
10 c.c. CrO_3 10% 10 c.c. NaCl 20%	45° Centigrade	43 Minutes.
"	" "	36 "
"	" "	39 "
"	" "	32 "
"	" "	41 "
10 c.c. CrO_3 10% 10 c.c. NaCl 20%	55° Centigrade	12 Minutes.
"	" "	7 "
"	" "	9 "
"	" "	12 "
"	" "	6 "

No time record was kept for temperatures above 55° centigrade, but the increase in solubility from this point on is not as great as up to this point. At a temperature of 100 centigrade the time required for the solution is about four minutes. The above tests, as those that follow were run on discs of gold leaf weighing .0004 grams

SOLUTION	TEMPERATURE	TIME
IO c.c. CrO_3 5% IO c.c. NaCl 20%	25° Centigrade	1 hour 51 minutes.
"	" "	1 " 58 "
"	" "	1 " 47 "
"	" "	2 " 3 "
"	" "	2 " 7 "

The temperatures in the last two cases dropped to about 20° Centigrade.

SOLUTION	TEMPERATURE	TIME
IOc.c. CrO_3 5 % IO c.c. NaCl 20%	35° Centigrade	1 hour 33 minutes.
"	" "	1 " 29 "
"	" "	1 " 37 "
"	" "	1 " 30 "
"	" "	1 " 33 "
IO c.c. CrO_3 5 % IO c.c. NaCl 20%	45° Centigrade	1 hour 9 minutes.
"	" "	1 " 12 "
"	" "	1 " 7 "
"	" "	1 " 7 "
"	" "	1 " 59 "

In the last case the temperature became a little higher than 45°.

SOLUTION	TEMPERATURE	TIME
I0 c.c. CrO_3 5 % I0 c.c. NaCl 20%	55° Centigrade	39 minutes.
"	" "	27 "
"	" "	22 "
"	" "	37 "
"	" "	29 "

When the salt solution was ten per cent and the chromium trioxide five per cent the time required for the entire solution of the disc of gold leaf is increased a very little.

SOLUTION	TEMPERATURE	TIME
10 c.c. CrO_3 5 % 10 c.c. NaCl 10%	25° Centigrade	2 hours 15 minutes.
"	" "	2 " 8 "
"	" "	2 " 17 "
"	" "	2 " 6 "
"	" "	2 " 9 "
I0 c.c. CrO_3 5% I0 c.c. NaCl 10%	35° Centigrade	1 hour 59 minutes.
"	" "	1 " 55 "
"	" "	1 " 47 "
"	" "	1 " 42 "
"	" "	1 " 53 "

SOLUTION	TEMPERATURE	TIME
IO c.c. CrO_3 5 % IO c.c. NaCl 10%	45° Centigrade	1 hour 27 minutes.
"	" "	1 " 32 "
"	" "	1 " 29 "
"	" "	1 " 36 "
"	" "	1 " 26 "
IO c.c. CrO_3 5% 10 c.c. NaCl 10%	55° Centigrade	57 minutes.
"	" "	52 "
"	" "	43 "
"	" "	49 "
"	" "	51 "
10 c.c. CrO_3 $2\frac{1}{2}$ % 10 c.c. NaCl 5 %	25° Centigrade	3 hours 37 minutes.
"	" "	3 " 29 "
"	" "	3 " 39 "
"	" "	3 " 32 "
"	" "	3 " 37 "

SOLUTION	TEMPERATURE	TIME
10 c.c. CrO_3 2½ % 10 c.c. NaCl 5 %	35° Centigrade	2 hours 57 minutes.
"	" "	2 " 51 "
"	" "	2 " 47 "
"	" "	2 " 51 "
"	" "	2 " 52 "
10 c.c. CrO_3 2½ % 10 c.c. NaCl 5%	45° Centigrade	1 hour 57 minutes.
"	" "	1 " 52 "
"	" "	1 " 58 "
"	" "	1 " 59 "
"	" "	1 " 55 "
10 c.c. CrO_3 2½% 10 c.c. NaCl 5%	55° Centigrade	1 hour 21 minutes.
"	" "	1 " 19 "
"	" "	1 " 24 "
"	" "	1 " 4 "
"	" "	1 " 7 "

The temperature went up to almost 65° in the last two cases.

At the temperature of the laboratory which was about 20 Centigrade the action of the solution of this concentration was very slow, about six hours being required to entirely dissolve the disc(.0004 grams) of gold leaf.

SOLUTION	TEMPERATURE	TIME
10 c.c. CrO_3 $1\frac{1}{4}\%$ 10 c.c. NaCl Sat.	55° centigrade	1 hour 49 minutes.
"	" "	1 " 58 "
"	" "	1 " 55 "
"	" "	1 " 49 "
"	" "	1 " 49 "
10 c.c. CrO_3 $1\frac{1}{4}\%$ 10 c.c. NaCl 20%	55° centigrade	2 hours 14 minutes.
"	" "	2 " 12 "
"	" "	2 " 9 "
"	" "	2 " 12 "
"	" "	2 " 13 "
10 c.c. CrO_3 .31 % 10 c.c. NaCl Sat.	55° Centigrade	2 hours 20 minutes.
"	" "	2 " 20 "
"	" "	2 " 17 "
"	" "	2 " 19 "
"	" "	2 " 17 "

SOLUTION	TEMPERATURE	TIME
10 c.c. CrO_3 .31 % 10 c.c. NaCl 10 %	55° Centigrade	4 hours 12 minutes.
"	" "	4 " 17 "
"	" "	3 " 52 "
"	" "	3 " 59 "
"	" "	3 " 57 "

In the last three cases the temperature went above 55 Centigrade

10 c.c. CrO_3 .31 % 10 c.c. NaCl 20 %	55° Centigrade	3 hours 43 minutes.
"	"	3 " 56 "
"	"	3 " 41 "
"	"	3 " 37 "
"	"	3 " 49 "

The strengh of the sodium chloride solution influences the mixture as does the strengh of the chromium oxide solution. The action being more rapid when a saturated solution of sodium chloride is used. The effect of foreign substances on the action of the solution was tried. Ferrous sulphide (FeS), antimony trisulphide (Sb_2S_3), arsenic trisulphide (As_2S_3) and potassium sulphide were introduced into the solution. The first three sulphides; ferrous sulphide, antimony trisulphide and arsenic trisulphide had very little evil influence on the solution; the speed of the reaction being decreased very little. In the case of the potassium sulphide the salt was dissolved and the solvent power of the solution entirely destroyed.

It may be inferred from this that soluble sulphides destroy the action of the solution. The influence of potassium and am-

monium persulphates was tried and it was found that they did not hasten the activity of the solution nor did they retard it.

Hydrogen peroxide does not accelerate the action. A few drops of acid increases the speed of reaction. The strengh of the solution did not deteriorate even after a number of gold discs had been dissolvedin it, but seemed to become more active after standing several days. This increase in activity was not due to the solution becoming more concentrated, as the solution was kept up to 20 c.c.

The question arises,-is the solvent action of this solution due to the formation of chlorine or is it an oxidizing reaction? Chromyl chloride (CrO_2Cl_2) was prepared by fusing ten parts of salt with seventeen parts sodium monochromate and then distilling with anhydrous sulphuric acid. Chromyl chloride is formed according to the following equation:

$$Na_2CrO_4+2NaCl+4H_2SO_4=CrO_2Cl_2\ 4NaHSO_4+2H_2O.$$ 6.

The water which is formed at the same time must be absorbed by the sulphuric acid, else the chromyl chloride will be decomposed. It was impossible to test the solvent action of chromyl chloride on gold because it could not be obtained free from chlorine. It is evident, however, that no chromyl chloride is formed in the solution from the fact that it decomposes according to the equation given below and that no free chlorine can be detected in the solution.

$$CrO_2Cl_2+H_2O=CrO_3+2HCl.$$ 6

No free chlorine can be detected by the odor or any chemical means and the fact that this solution is used to dissolve gold off platinum electrodes shows that free chlorine is not present.

Free chlorine attacks platinum forming platinic chloride ($PtCl_4$). A suggested explanation is as follows:

The solvent action of this solution is due to oxidization and the fact that the oxide of gold is soluble in acid. The reaction which takes place when a solution of chromium trioxide and sodium chloride are brought together is represented by the following equations:

6 $CrO_3+H_2O=H_2CrO_4$

$H_2CrO_4+2NaCl=Na_2CrO_4+2HCl$

$2Na_2CrO_4+2HCl=2NaCl+Na_2Cr_2O_7+H_2O$

$Na_2Cr_2O_7+8HCl=Cr_2Cl_6+2NaCl+4H_2O+3O$

It is the free oxygen in the last equation which attacks the gold.

Chromium trioxide when brought in contact with water forms chromic acid (H_2CrO_4).

That hydrochloric acid is formed in the following equation is proven by the fact that the acid can be distilled off and condensed.

6. $H_2CrO_4+2NaCl=Na_2CrO_4+2HCl.$

A mixture of chromium trioxide solution and salt solution was put in a distilling flask connected with a bottle, through which the vapors first passed, and a condenser. This bottle between the distilling flask and the condenser was to catch any solid particles that might be carried over. The distillate gave a white precipitate when treated with silver nitrate ($AgNo_3$). This precipitate was silver chloride ($AgCl$). The distillate turned blue litmus paper red. These tests prove that hydrocloric

acid is formed in the mixture. All necessary precautions were taken to prevent any salt or chromic acid from being carried over into the distillate. The solution before distilling was treated with barium hydroxide to precipitate any sulphuric acid that might be present. The solution of chromium trioxide was tested for hydrochloric acid before the sodium chloride was added. No hydrochloric acid was present.

The mixture of chromic oxide solution and sodium chloride solution was run on various ores to determine the percentage of extraction and the effect of the various impurities in the ore on the solution.

The first ore run was a talcose ore, a hydrated silicate of magnesia ($3MgO\ 4SiO_2H_2O$) The gold in this ore existed in a free state in minute particles, some being large enough to be seen with the naked eye. The ore was put through a forty mesh sieve before treatment. Two A.T. of the ore were taken and treated for two hours with the mixture at a temperature of 55°. The following data being taken, a solution of sodium thiosulphate ($Na_2S_2O_3$) the value of which is known in terms of chromium trioxide, being used for the titrations.

10 c.c. Solution before treating ore =20.9 c.c. $Na_2S_2O_3$.

10 c.c. After treatment of ore =19.1 c.c. "

1 c.c. $Na_2S_2O_3$ = .00512 grams CrO_3

20.9 c.c. $Na_2S_2O_3$ X .00512 grams CrO_3 .107008 grams CrO_3

19.1 c.c. " X .00512 " " .097791 " "

.009217

.009217 grams CrO_3 loss due to the action of the ore.

.009217 grams loss ÷ .107008 grams initial strengh of solution

equals .09. The per cent of deterioration is 9 %. The gold was precipitated from the solution by means of a few grams of mercury. A brownish coating is formed over the mercury when it is used for precipitating the gold. The coating consists of the oxides of mercury. The solution was drawn off, the mercury washed and then treated with nitric acid. The gold remained as a black amorphous powder. The gold after heating in an annealing cup weighed .00220 grams. The ore by fire assay showed a value of .00116 grams. As two assay tons were taken this shows an extraction of .00110 grams. The solution after the gold was precipitated was evaporated and assayed. A trace of gold remained in solution.

The ore after treatment was dried and assayed. It showed trace of gold remaining undissolved. The solution after treatment with mercury was titrated against the sodium thiosulphate to determine the deterioration caused by the mercury.

10 c.c. Solution after treatment of ore=19.1 c.c. $Na_2S_2O_3$
10 c.c. After precipitation with mercury=17.9 c.c. $Na_2S_2O_3$
19.1 c.c.$Na_2S_2O_3$ X .00512 grams CrO_3 =.097791 grams CrO_3
17.9 c.c. " X .00512 " " =.091648 " "
.006143

.006143 grams CrO_3 loss due to the action of mercury .
.006143 grams loss ÷.097791 grams CrO_3 equals .06 or 6 %.

In this case the total loss of strength due to the action of the ore and the mercury equals 15 %.

Ore number eighteen was treated with a mixture of chromium oxide solution and salt solution. This ore is a sulphuret concentrate. The ore was treated both before and after roasting.

Before roasting:

10 c.c. CrO_3 solution before treating ore = 24 c.c. $Na_2S_2O_3$
10 c.c. " " after " " = 9.35 c.c. "

24 c.c. CrO_3 $Na_2S_2O_3$ X .00512 grams CrO_3 = .12288
9.35 c.c. CrO_3 " X .00512 " " = .04787
.07501 loss

.07501 grams CrO_3 loss .12288 grams CrO_3 in original solution .61 or 61 %. The large per cent of deterioration is due to the fact that the solution oxidized the large amount of sulphur in the ore. The solution acted on the ore for two hours at 55° Centigrade. After filtering the solution was evaporated and assayed. 0012 grams of gold was obtained. The ore assays .0063 grams. This low extraction was due to the fact that the solution was consumed in oxidizing the sulphuret. This same ore was roasted and then treated with the solution.

After roasting:

10 c.c. CrO_3 solution before treating ore = 24 c.c. $Na_2S_2O_3$
10 c.c. " " after " " = 19.7 c.c. "

This ore was treated for two hours at a temperature of 55° Centigrade.

24 c.c. $Na_2S_2O_3$ X .00512 grams CrO_3 = .12288 grams CrO_3
19.7 c.c. " X .00512 " " = .10086 " "
.02202

.02202 grams CrO_3 loss ÷ .12288 grams CrO_3 ariginal strength of solution equals .179 or 17.9 %.

The percent of loss is high, but is no doubt due to the fact that some of the sulphur was not oxidized by the roasting. The gold was precipitated from the solution by means of mercury.

After precipitation with mercury:

10 c.c. solution after treating ore =19.7 c.c. $Na_2S_2O_3$

10 c.c. " " precipitation with mercury =17.9c.c.$Na_2S_2O_3$

19.7 c.c. $Na_2S_2O_3$ X .00512 grams CrO_3=.100864 grams CrO_3
17.9 c.c. " X .00512 " " =.091648 " "
.009216 loss

.009216 grams CrO_3 loss÷.10086 grams CrO_3 the strength of solution after treating ore equals .091 or 9.1 per cent.

The extraction from the solution by means of mercury was .00575 grams. The solution after precipitation was evaporated and assayed .0004 grams of gold were obtained. The sum of these two weights give the total extraction of the solution.00615 grams, being the total extraction. The ore after treatment was dried and assayed and showed a trace of gold. Ore 18 assays.0063 grams per ton. This gives an extraction of 97 %.

A free milling ore with quartz gangue carrying a little iron pyrites was run and the following results were obtained:

Ore number 16 in ore cabinet:

10 c.c. solution before treating ore 20.0 c.c. $Na_2S_2O_3$
10 c.c. " after " " 16.2 c.c. "

20.0 c.c.$Na_2S_2O_3$ X .00512 grams CrO_3=.10240 grams CrO_3
16.2 c.c. " X .00512 " " =.08294 " "
.01946 loss

.01946 loss in grams of CrO_3÷.10240 grams CrO_3 the original concentration equals .190 or 19 %. This large per cent of loss is probably due to the fact that the gangue of the ore carried some iron pyrites. Mercury was not used to precipitate the gold from the solution in this case, but the solution was assayed after

evaporation .00474 grams of gold were obtained. The assay value of the ore is .00529 grams of gold per ton. This is an extraction 91 %. No account was taken of the silver. Time two hours, temperature 55 Centigrade.

A copper matte was treated with the solution, both before and after roasting with the following results:

Before roasting:

10 c.c. of solution before treating ore = 18.3 c.c. $Na_2S_2O_3$
10 c.c. " " after " " = 0.8 c.c. "

18.3 c.c. $Na_2S_2O_3$ X .00512 grams CrO_3 .09369 grams CrO_3
0.8 c.c. " X .00512 " " .00409 " "
.08960 loss

.08960 loss in grams of CrO_3 ÷ .09369 grams CrO_3 the original concentration of the solution equals .958 or 95.8 %.

The large per cent of deterioration in the treatment of this ore was caused by the sulphur in the matte. A large quantity of oxygen being necessary to oxidize it. The solution after being filtered from this ore had a blue color owing to the copper dissolved in it.

After roasting:

10 c.c. of solution before treating ore 18.3 c.c. $Na_2S_2O_3$
10 c.c. " " after " " 17.1 c.c. "

18.3cc. $Na_2S_2O_3$ X .00512 grams CrO_3 .09369 grams CrO_3
17.1cc. " X .00512 " " .08753 " "
.00616 loss

.00616 loss in grams of CrO_3 ÷ .09369 grams CrO_3 the original concentration of the solution .064 or 6.4 per cent. The percentage of deterioration would probably have been smaller

had the roast been complete. The solution was evaporated and assayed. The bead obtained weighed .05964 grams. As two assayed tons were used the extraction in ounces per ton was 29.82 ounces. The bead was parted and but a slight trace of gold was obtained. This matte assays .0339 grams of silver and a trace of gold per ton. The ore after treatment was assayed and there remained unextracted .05329 grams of silver. This gives and extraction of 35.5 per cent of silver. This ore was treated for two hours at a temperature of 55° Centigrade.

From this test it appears that silver chromate which is formed is soluble in a mixture of chromium trioxide and salt up to a certain limit. A few drops of dilute silver nitrate were added to the mixture and no precipitate appeared. When more silver nitrate was added a yellowish precipitate was thrown out. This shows that the mixture will dissolve a certain amount of silver, but when an excess is present, the insoluble silver chromate is formed.

Ore number 15, a pyritic concentrate gave the following data when treated with the solution. The ore was treated both before and after roasting.

Before roasting:

10 c.c. solution before treating ore = 24 c.c. $Na_2S_2O_3$
10 c.c. " after " " = 7.25 c.c. "

24 c.c. $Na_2S_2O_3$ X .00512 grams CrO_3 = .12288 grams CrO_3
7.25 c.c. " X .00512 " " = .03712 " "
.08576 loss

.08576 grams CrO_3 loss ÷ .12288 grams CrO_3 the original strength of solution equals .680 or 68 %. The sulphur in the ore consumed a great deal of the oxygen, consequently the strengh of the solution was very much reduced. The solution was evaporated and

assayed. The bead weighing .00217 grams was obtained. The ore after this treatment, when assayed gave a bead weighing .00329 grams. This gave .00548 grams as the assay value of the ore. The ore assays .00554 grams per assay ton. This represents an extraction of 59.2 per cent. This extraction was low because the ore was not roasted and a considerable quantity of the solution was consumed in oxidizing the sulphur. The extraction represents the free gold; the gold on the sulphide not being attacked by the solution.

After roasting:

10 c.c. solution before treating ore = 24 c.c. $Na_2S_2O_3$
10 c.c. " after " " = 21.7 c.c. $Na_2S_2O_3$

24 c.c. $Na_2S_2O_3$ X .00512 grams CrO_3 = .12288 grams CrO_3
21.7 c.c. " X .00512 " " = .11110 " "
.1178 loss.

.01178 grams CrO loss ÷ .12288 grams CrO_3 the original strength of the solution equals .095 or 9.5 %. This deterioration may be partly due to the roast not being complete. The solution was treated with finely divided calcium oxide (CaO). The gold was carried down by the lime. After being agitated for a few minutes the solution was filtered, the lime dried and assayed. A bead weighing .00497 grams was obtained. This bead did not contain enough silver to part. The solution was evaporated and assayed. The bead obtained was too small to weigh. Taking the total extraction as .00497 we have 88.7 as the percentage of extraction. The ore after treatment when assayed gave a bead weighing .00039 grams. The solution after treatment with the calcium oxide showed a very slight deterioration.

The following data was obtained when a decomposed porphyry was treated with the mixture. This porphyry was stained with iron oxide.

10 c.c. solution before treating ore = 24 c.c. $Na_2S_2O_3$

10 c.c. " after " " = 10 c.c. "

24 c.c. $Na_2S_2O_3$ X .00512 grams CrO_3 = .12288 grams CrO_3

10 c.c. $Na_2S_2O_3$ X .00512 " " = .05120 grams CrO_3

.07168 loss

.07168 grams of CrO_3 loss ÷ .12288 grams CrO_3 initial strength of solution equals .05830 or 58.3 %. This large percentage of loss is probably due to the presence of iron in the ore which consumed the oxygen. The solution was evaporated and assayed, a bead weighing .02842 grams being obtained. This bead parted readily and gold weighing .001 grams remained. The ore after treatment when assayed gave a bead weighing .02426 grams. A trace of gold was left when this bead was parted. The ore assays .0014 grams of gold and .05188 grams of silver per assay ton. The percentage extraction of gold is 71.4 and that of silver is 46.7.

The low extraction is accounted for in this case by the fact that the strength of the solution was reduced by the iron present in the ore. The silver extraction was low also from the fact that there was an excess of silver in the ore.

Ore number six, a silicious sinter, was treated with a mixture of chromic trioxide solution and salt solution. Silicious sinters are deposited by heated waters in the form of a gelatinous mass which becomes porous on drying. The heated waters carry metals in solution which are deposited with the sinter.

The following data was obtained:

10 c.c. solution before treating the ore = 24 c.c. $Na_2S_2O_3$

10 c.c. " after " " " = 21.7 c.c. "

24 c.c. $Na_2S_2O_3$ X .00512 grams CrO_3 = .12288 CrO_3

21.7 c.c. $Na_2S_2O_3$ X .00512 " " = $\underline{.111104}$ "

.01178 loss.

.01178 grams CrO_3 loss ÷ .12288 grams CrO_3 original strength of solution equals .095 or 9.5 %. The sinter appears to be stained with iron which would consume some of the oxygen liberated, thus causing a larger percentage decrease. The solution was evaporated and assayed. A bead weighing .02824 grams was obtained. This was parted and the gold weighed .00084 grams. The weight of silver obtained by difference being .0274 grams. The above figures give the weights per assay ton. The ore by fire assay gives .00092 grams of gold and .05252 grams of silver per ton. The extraction of gold was 91.3 % and that of silver was 52.1 %. The ore after treatment was assayed. A slight trace of gold being obtained and .0248 grams of silver.

A carbonate gangue carrying free gold and gold telluride was run with the solution with the following results:

10 c.c. solution before roasting ore = 13 c.c. $Na_2S_2O_3$

10 c.c. " after " " = 10.4 c.c. "

13 c.c. $Na_2S_2O_3$ X .00512 grams CrO = .06656 grams CrO_3

10.4 c.c. " X .00512 " " = $\underline{.05324}$ " "

.01332 loss.

.01332 grams CrO_3 loss ÷ .06656 grams CrO_3 original strength equals .20 or 20 %. The solution was evaporated and assayed, no bead being obtained. The extraction in this case was zero.

This ore was run with out roasting. It probably carries no free gold and the solution did not attack the telluride. This accounts for the fact that no extraction was obtained. Lack of time prevented this ore from being tested after roasting.

Recovery of gold from Chromic Acid Solution:

The precipitation or removal of the gold from the solution is a problem which naturally follows the solution of the gold. The two most effective reagents for removing the gold from the solution are mercury and calcium oxide.

Mercury on being shaken with the solution removes the gold, which is left behind as an amorphous powder when the mercury is distilled. The mercury has a bad effect upon the solution, the strength of which deteriorates from 6 to 10 % according to the length of time the mercury is left in contact with it. The removal of the gold is not complete, a slight trace remaining.

Calcium oxide throws the gold out of the solution as a black amorphous powder. A number of tests which follow show the effect of the oxide on the solution. Zinc removes the gold but destroys the solution. Neither oxalic acid nor ferrous sulphate would throw the gold out of solution.

A series of tests was run to determine the effect of calcium oxide on the mixture of chromium trioxide solution and salt solution. The following results were abtained:

10 c.c. solution before treatment with $CaO = 17.1$ c.c. $Na_2S_2O_3$
10 c.c. " after " " " $= 16.8$ c.c. "
Deterioration 1.7 per cent.

10 c.c. solution before treatment with CaO = 17.1 c.c. $Na_2S_2O_3$
10 c.c. " after " " " = 16.5 c.c. "
Deterioration 3.5 per cent.

10 c.c. solution before treatment with CaO = 17.1 c.c. $Na_2S_2O_3$
10 c.c. " after " " " = 16.8 c.c. "
Deterioration 1.7 per cent.

The three tests give an average of 2.3 per cent of deterioration. The above tests were run for thirty minutes at the temperature of the laboratory.

The next three tests were run for an hour at a temperature of about 20° Centigrade.

10 c.c. solution before treatment with CaO = 17.2 c.c. $Na_2S_2O_3$
10 c.c. " after " " " = 16.6 c.c. "
Deterioration 3.2 per cent.

10 c.c. solution before treatment with CaO = 17.2 c.c. $Na_2S_2O_3$
10 c.c. " after " " " = 16.4 c.c. "
Deterioration of 4.2 per cent.

10 c.c. solution before treatment with CaO = 17.2 c.c. $Na_2S_2O_3$
10 c.c. " after " " " = 16.4 c.c. "
Deterioration of 4.2 per cent.

The average deterioration is 3.8 per cent.

After running forty-eight hours at the temperature of the laboratory the following titrations were made:

10 c.c. before treatment with CaO = 17.2 c.c. $Na_2S_2O_3$
10 c.c. after " " " = 16.3 c.c. $Na_2S_2O_3$
Deterioration 5.2 per cent.

10 c.c. solution before treating with CaO = 17.2 c.c. $Na_2S_2O_3$

10 c.c. " after " " " = 16.0 c.c. "

Deterioration 8.1 per cent.

10 c.c. solution before treatment with CaO = 17.2 c.c. $Na_2S_2O_3$

10 c.c. " after " " " = 16.1 c.c. "

Deterioration 6.3 per cent.

Average deterioration 6.5 per cent.

To determine the effectiveness of calcium oxide as a precipitation agent for the gold in the mixture .0015 grams of gold were dissolved in 25 c.c. and then treated with calcium oxide. After being stirred for a few minutes the lime was filtered off, dried and assayed. A gold bead weighing .00132 grams was obtained. The solution was evaporated and assayed and .00016 grams of gold were obtained from it. 88 % of the gold was precipitated. The solution showed a very slight deterioration.

.00292 grams of gold were dissolved in 25 c.c. of the solution and precipitated with lime. On assaying the CaO .00254 grams of gold were obtained. The solution when evaporated gave a bead weighing .00034 grams. The precipitation in this case was 87 per cent.

The electric current was tried for precipitating the gold from the solution. With a current of from .3 to .6 amperes, a voltage of from 6 to 8 volts and a rotating cathode, the following results were obtained:

Weight of cathode 13.9838 grams.

" " cathode with gold deposited 13.9856 grams.

" " gold deposited .0018 grams.

" " " in solution .0031 grams.

Percentage of extraction 58.06.

The solution after electrolysis contained chlorine and deteriorated about 17 %. A few grams of zinc sulphate were added to increase the conductivity of the solution. Lack of time prevented more work being done along this line.

In the above experiments the chemical reactions and the speed of action were noted and no time was spent in determining the practicability of the process. It would be interesting and profitable to work along this line if time would permit.

(1) The Principles of Metallurgy.

Horn.

(2) The Cyanide Process, It's Practical Applications and Economical Results. Page 9.

Dr.A.S.Scheidel E.M.

(3) Practical Notes on the Cyanide Process. Page 1.

Bosqui.

The Cyanide Process for the Extraction of Gold. Page 65.

Eissler.

(4) Gold Extraction by Cyanide. MacArthur.

Journal of the Society of Chemical Industry.

No.7, Vol.XXIV, Page 311-315.

(5) Solubility of Gold in Certain Oxidizing Agents

Victor Lenher.

Journal of the American Chemical Society.

No.5, Vol.XXVI, Page 550.

(6) This equation has been previously worked out and may be found in any good text book of Inorganic Chemistry.

(7) This reagent was tested by Lenher.

(8) Studied for this thesis.

(9) Quantitative Chemical Analysis by Electrolysis. Page 177.

Classen.

The work on the solvents for gold has been quite extensive but as the results have not been entirely satisfactory little has been published along this line. The following works have been written on the solubility of gold:

(1) The Cyanide Process for the Extraction of Gold.
Eissler.

(2) Practical Notes on the Cyanide Process.
Bosqui.

(3) The Metallurgy of Gold. Eissler.

(4) Metallurgy of Gold, Silver and Mercury in the United States. Egleston.

(5) Solubility of Gold in Certain Oxidizing Agents.
Lenher.
Journal American Chemical Society.
No.5, Vol. XXVI, Page 550.

(6) Gold Extraction by Cyanide. MacArthur.
Journal of the Society of Chemical Industry.
No.7, Vol. XXIV, Pages 311-315.

(7) The Principles of Metallurgy. Horn.

(8) The Cyanide Process, It's Practical Applications and Economical Results. Dr.A.S.Scheidel E.M.